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(54) Title: HYDROCARBON GELS USEFUL IN FORMATION FRACTURING

(57) Abstract

This invention relates to improved hydrocarbon gels finding use in the fracturing of formations which produce petroleum and other hydrocarbons. The gelling agents comprise combinations of ferric salts, selected orthophosphate esters, triethonolamine or triethylamine, and a surfactant.

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HYDROCARBON GELS USEFUL IN FORMATION FRACTURING

Related Applications

This application is a continuation-in-part of our application SN 08/360,438 of the same title filed December 21, 1994, which is a division of our application SN 08/209,266, also of the same title, filed March 14, 1994, now US Patent 5,417,287.

Technical Field

This invention relates to improved hydrocarbon gels which find use in petroleum producing formation fracturing. In particular it relates to the use of a defined class of gelling agents for hydrocarbons which provide excellent results in such fracturing.

The gelling agents are combinations of ferric salts; low molecular weight amines, and selected orthophosphate esters with or without optional surfactants.

Background of the Invention

The development of the use of gelled hydrocarbons as fracturing fluids is reviewed by Weldon M. Harms in a chapter entitled "Application of Chemistry in Oil and Gas Well Fracturing", at pages 59-60 of the book "Oil-Field Chemistry (ACS Symposium #396 - 1988)" published by the American Chemical Society in 1989. The basic technique of formation fracturing involves the injection of a fracturing fluid down the well bore, which is usually cemented in place and at least 0.3 mile long, and then

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through horizontal holes in the steel pipe, or casing, of the well, to obtain access to the subterranean formation. The fracturing fluid is under high pressure and must be able to survive the severe shear forces caused when flow is forced through the casing perforations of perhaps ¼ to ½ inch in diameter, as well as the shear forces encountered at the leading edge of the fracture. Whatever chemical additives are used to influence viscosity, induce gel formation, stabilize against resident chemicals, pH or temperature conditions in the formation, inhibit scale formation or corrosion, or inhibit paraffin deposition, for example, must also be able to withstand the shear forces and other inhospitable conditions of use. Most commonly available liquids typically are viscosified before they are particularly effective in carrying the large quantities of proppants widely used in the fracturing process.

When hydrocarbons are used in the fracturing process, they are commonly treated to increase their viscosity. As reviewed by Harms, an early viscosifying agent was napalm, an aluminum soap of fatty acids. Aluminum salts of orthophosphate esters were introduced in the late 1960's, followed by the suggestion of the use of Fe_3O_4 for combination with the orthophosphate esters, in Monroe US Patent 3,505,374. While many other combinations of metals and other materials have been suggested as viscosifying agents, aluminum crosslinked orthophosphate esters are still, according to Harms, the most widely used.

The aluminum compounds present problems, however, particularly where any significant amount of water is

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present. They generally will not satisfactorily perform
the desired crosslinking function in the presence of more
than about 1200 ppm of water, nor where the pH is outside
a relatively narrow range. Moreover, an inadvertent
excess of aluminum compound treatment is detrimental to
the desired performance because the aluminum compound
itself adversely affects the pH. The iron provided by
ferric salts as in the present invention, on the
contrary, permits operation in wider pH ranges.

In describing a gel which can be used as a pig in a
pipeline, Jaggard et al in US Patent 4,003,393 recite the
possibility of iron as one of a number of metals to
combine with a class of aliphatic substituted
orthophosphoric esters. No other qualifiers are used to
describe the iron, however.

In US Patent 4,153,649, Griffin proposes reacting a
pentavalent phosphorous compound with a class of hydroxy
ethers before employing the metal salt. Among the metal
salts he uses is ferric nitrate, but he further requires
a "separate source of base" to be used with the hydroxy
ether modified phosphates, as spelled out in column 4,
lines 55-58 and column 11, lines 37-68.

Monroe, in US Patent 3,505,374, uses a gelling agent for
hydrocarbons characterized as a ferroso-ferric salt of an
alkyl oleyl diester of orthophosphoric mono acid. The
iron compound is further described as magnetite, or
Fe_3O_4. He suggests this combination for fracturing
subterranean oil-bearing formations, but says none of the
"other oxidized forms of iron including ferrous and
ferric oxides and hydroxides, chlorides, sulfates and

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nitrates" (col 3, lines 2-4) yielded a gel as obtained with the magnetite.

Burnham, in US Patent 4,200,540, describes a large class
5   of phosphates and phosphate esters which he mixes with aluminum salts, aluminates and aluminum metal. He chooses combinations of the materials as a function of various down-hole temperatures. No mention is made of iron salts; the reference is cited mainly for its
10   comprehensive description of the phosphates deemed to be useful. See also Burnham's US Patent 4,316,810.

Summary of the Invention

15   We have found that ferric salts can be very advantageously used in the gelling of hydrocarbons, particularly for use in formation fracturing, rather than aluminum compounds, for combination with orthophosphate esters.

20
The ferric salt has the advantage that it can be used in the presence of large amounts of water, such as up to 20%. One of the advantages of fracturing with hydrocarbon gels is that some formations may tend to
25   imbibe large quantities of water, while others are water-sensitive and will swell inordinately if water is introduced; our invention permits one to use a hydrocarbon gel in areas where water may cause trouble not only with the formation itself, but with the
30   fracturing agent or the gelling agent. Also, it is not adversely affected by commonly used alcohols, such as methanol and isopropanol. In addition, it can be used in broad ranges of pH, yet the linkages it forms can still

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be broken with gel breaking additives conventionally used for that purpose. In addition, ferric salts such as ferric sulfate crosslink rapidly and can be made to link even more rapidly with the use of surfactants and/or alkaline or caustic agents such as potassium hydroxide. This continuation-in-part application is directed specifically to combinations of the ferric salts, particularly ferric sulfate, with low molecular weight amines such as triethylamine and triethanolamine, referred to herein sometimes interchangeably as TEA. Other low molecular weight amines useful in our invention are within the generic description found elsewhere herein and include monoisopropanol, butyl amine, and hexyl amine.

When dissolved in a hydrocarbon such as gasoline, diesel oil, crude oil, or kerosene, the ferric salt in combination with orthophosphate esters as defined below will cause the hydrocarbon to gel. The gel is generally stable to heat, and the degree of gelling can be controlled by the concentration of orthophosphate ester in the fluid.

Detailed Description of the Invention

The phosphate ester which we use is advantageously added first and mixed with the Diesel fuel or other hydrocarbon to be used as the fracturing agent, generally in amounts from about 0.3% to about 1.5% by weight, based on the total. Then the ferric salt is added in amounts to provide preferably about one mole of ferric iron for each mole of phosphate or phosphate ester. In this manner, the process materials can be prepared more or less

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continuously, as opposed to the batch approach sometimes
used in the past. More broadly we may use any amount of
ferric salt which is effective to make a gel with the
phosphate ester. This will be accomplished at about 0.1
5   to about 1.5 mole of ferric iron for each mole of
phosphate ester, preferably 0.8:1 to 1.2:1.

A low molecular weight amine is also employed. The low
molecular weight amine is preferably one of the formula
10   $N(CH_2CH_2R)_3$, where R is H or OH, but may be any amine of
the formula $H_{3-n}N(C_mH_{2m}R)_n$ where m is an integer from 2 -
6, and n is an integer from 1 - 3, the alkylene group
represented by C_mH_{2m} may be linear or branched. Further
examples of such compounds are diisopropylamine,
15   triisobutylamine, and pentylamine.

The low molecular weight amine is advantageously first
mixed with the ferric salt in a molar ratio of ferric
salt to amine of about 0.25:1 to about 6:1. This is
20   accomplished by thorough blending.

We have also found that surfactants have the effect of
decreasing the time for crosslinking. Generally, in the
absence of a surfactant, our combination of materials
25   will crosslink in about two minutes at room temperature;
when a surfactant is used also, this time is
significantly reduced, and in the presence of our
preferred class of surfactants, it is reduced to the
neighborhood of twenty seconds, as determined by
30   viscosity tests. About 0.1% to about 10% (based on the
gelling agent) of surfactant is frequently advantageous
also.

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The phosphate derivatives we use are described in the literature as orthophosphate esters. They are similar to those used by Burnham in US Patents 4,200,540 and 4,316,810, Griffin in US Patents 4,174,283 and 4,153,649, and Harris et al in US Patent 4,622,155, having the structural formula
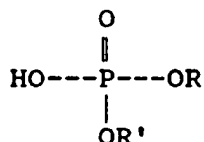
$$HO{-}{-}{-}\overset{\displaystyle O}{\overset{\displaystyle \|}{\underset{\displaystyle \underset{\displaystyle OR'}{|}}{P}}}{-}{-}{-}OR$$

where R is a straight or branched chain alkyl, aryl, alkoxy, or alkaryl group having about 6 to about 18 carbon atoms and R' is hydrogen or an aryl, alkaryl, alkoxy, or alkyl group having up to about 18 carbon atoms. This structural formula will be referred to elsewhere herein as HPO_4RR'.

In the fracturing fluid, the iron from the ferric sulfate or other ferric salt forms linkages with the available oxygen, generally in more than one phosphate group, thus forming small chains which cause the hydrocarbon to gel.

It has been demonstrated in the laboratory that our invention may be used to form hydrocarbon gels, and that the gels can be broken in a manner familiar to persons who work with hydrocarbon gels in the field such as by the addition of common alkaline materials. In the following examples, and in the results reported in Tables I - IV, the procedure was to employ a laboratory Waring blender with a voltage regulator set at 25. 300 ml of Diesel oil was placed in the blender and the power turned on. The phosphate ester preparation was first added and after it was blended, the ferric salt solution was introduced by pipette. The time was recorded from the

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initial introduction of the ferric compound to the gel
point, determined by a concave shape of the material in
the blender. Blending was continued to determine the
time required to reach maximum gel, which was estimated
5   to be the first sign of conversion of the shape of the
material to convex instead of concave. The blending was
then stopped and the material transferred to a sample
container, observing the consistency of the gel.
Brookfield viscosity readings were then taken as shown in
10   the Table I.

In the examples below, Composition M is about two-thirds
phosphate ester of the above formula HPO_4RR', together
with 10% triethanolamine, and solvent. Composition L
15   contains about two-thirds phosphate ester HPO_4RR',
together with 10% triethylamine, and high flash aliphatic
solvent. Composition K is two-thirds of the same
phosphate ester and 15.5g 45%KOH, also with a solvent.
Composition F contains about 27% ferric sulfate, together
20   with ethylene glycol, mixed surfactants, 10%
triethanolamine, and water. In each case, the amounts of
composition M shown were added first to the Diesel oil
and blended; then the amount shown of Composition F was
added and blended. Results are presented in Table I.

25   **Table I**

Ex	M	F	X-link	Invers	Spindl	5min	30min	60min
1	3ml	3ml	20 sec	30 sec	#3	2500	–	3890
2	3ml	3ml	20 sec	30 sec	#3	2300	–	3460
3	3ml	3ml	25 sec	35 sec	#3	2375	–	3400
4	3ml	3ml	30 sec	60 sec	#4	6360	11000	13800
5	3ml	3ml	30 sec	55 sec	#4	7320	12300	13500
6	3ml	3ml	45 sec	none at 180 sec				
7	2ml	2ml	60 sec	150 sec	#4	–	–	–
8	3ml*	3ml	20 sec	55 sec	#3	10000[l]	–	13000[l]
9	6ml*	3ml	15 sec	30 sec	#4	–	–	21500[l]
10	2ml$	3ml	20 sec	35 sec	#4	13650[l]	–	13850[l]

*   Composition L used instead of M
$ Composition K used instead of M   [l]   rotation at 10 rpm

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Persons skilled in the art will recognize from Table I that the formulations make excellent gels.

In a separate experiment, it was shown that the order of addition of the phosphate ester solution (sometimes herein called the gellant) and the ferric sulfate component (activator) is not important. In this experiment, 6.16g deionized water and 1.3g ferric sulfate were added to 85.95g Diesel oil and mixed with the blender; then 0.4 ml of phosphate esters of the formula HPO_4RR' was added and inversion took place in about one minute.

The data in Table II demonstrate that our hydrocarbon gel former will operate in the presence of significant amounts of water; indeed the viscosity increases with increasing amounts of water. In this experiment, an initial mixture was made as above with 4g of gellant and 10g of activator in about 250g of Diesel oil. Water was then added incrementally and the viscosity measured immediately.

Table II

Cumulative Water, %	Viscosity ($511\ sec^{-1}$)
0.65%	1cp
1.27%	6cp
2.16%	12cp
2.78%	19cp
3.50%	26cp
4.18%	29cp
5.06%	30cp
6.17%	*
7.58%	*
8.38%	*
10.41%	*
14.78%	*
20.2 %	*

*   Dial bouncing and unreadable; excellent lipping gel observed.

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Additional tests were made as shown in Table III, which records the viscosities achieved by various combinations within our invention.

Table III

ml M	ml F	cps	ml other	comment
3	3	13,800		
3	3	13,500		
2	2	(bouncing dial)		
a	3	13,000		
b	3	21,500	6TEA*	
c	3	13,900	2KOH	
3	3	15,000		
3	3	16,000		
d	3	5,800	low acid value PE	
e	3	9,400	high acid value PE	
f	3	20,800	KOH	
g	3	11,300	½KOH	
3	3	7,000	¼KOH	
3	3	8,600	no TEA in F	
3	3	8,700	KOH in M; no TEA in F	
3	3	14,500	KOH in M; no TEA	
3	3	13,400		
3	3	-	4400 cps @ 20 rpm	
i	3	9,300		
j	3	20,400		
2 ml	3	12,700		
2 ml	1.5	8,300		
k	1.5	10,000		
l	1.5	12,500	2 ph est; KOH; 1.5 Fe	
3	3	14,700		
m	3	20,000		
3	3	23,000	0.25g Na$_2$CO$_3$	
n	3	21,000		
o	3	18,400	0.25g Na$_2$CO$_3$	
3	3	19,500	0.5g CaCl$_2$	
p	3	13,800	0.5g CaCl$_2$	
2	3	7,000		
q	3	11,600		
r	3	12,100		
3	3	10,500		
3	3	10,500	Fe Citrate	
3	3	9,700		
3	3	6,800	Fe Citrate	
u	3	8,200		
v	3	18,400	Na$_2$CO$_3$	
w	3	21,000	Na$_2$CO$_3$	
x	3	10,000		
y	3	11,000		
aa	2	6,700		
bb	1	780		
cc	4	12,300		
dd	3	13,000		
ee	4	12,200		
ff	5	12,000		
gg	6	11,500		

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hh	7	12,300
ii	9	11,500
jj	11	11,400
kk	13	13,300
ll	17	11,800
mm	3	10,900
nn	3	14,700
oo	2	14,900
pp	4	14,900
qq	6	12,500
rr	8	12,700
ss	11	10,400
tt	15	7,600

In Table II, the following notes apply to the column headed "ml Other":

a   triethylamine with phosphate ester of M -- 3 ml
b   triethylamine with phosphate ester of M -- 6 ml
c   KOH with phosphate ester of M -- 2 ml
d   triethanolamine with varied phosphate ester -- 3 ml
e   triethanolamine with varied phosphate ester -- 3 ml
f   KOH with phosphate ester of M -- 3 ml
g   same as f with half as much KOH -- 3 ml
h   same as g with half as much KOH -- 3 ml
i, m, n, o, p   KOH with phosphate ester of M -- 3 ml
k, l   KOH with phosphate ester of M -- 2 ml
q, r, s   KOH with varied phosphate ester -- 2 ml
t,u,v,w,x,y   no alkali; phosphate ester of M -- 3 ml
aa   3 ml non-neut phosphate ester; 2ml F
bb   3 ml non-neut phosphate ester; 1 ml F
cc   3 ml non-neut phosphate ester; 4 ml F
dd   3 ml KOH-treated phosphate ester; 3 ml F
ee   3 ml KOH-treated phosphate ester; 4 ml F
ff   3 ml KOH-treated phosphate ester; 5 ml F
gg   3 ml KOH-treated phosphate ester; 6 ml F
hh   3 ml KOH-treated phosphate ester; 7 ml F
ii   3 ml KOH-treated phosphate ester; 9 ml F
jj   3 ml KOH-treated phosphate ester; 11 ml F
kk   3 ml KOH-treated phosphate ester; 13 ml F
ll   3 ml KOH-treated phosphate ester; 17 ml F
mm   3 ml non-neut phosphate ester; 3 ml F
nn   3 ml non-neut phosphate ester; 2 ml F
oo   3 ml M; 4 ml F
pp   3 ml M; 6 ml F
qq   3 ml M; 8 ml F
rr   3 ml M; 11 ml F
ss   3 ml M; 15 ml F
*   6 ml of triethanolamine instead of 3 ml

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From the above table III, it is apparent that a broad
range of ferric salts, neutralizing agents, and other
additives such as breakers, and other materials are not
detrimental to the gelling abilities of our invention.
In addition, it may be seen that triethanolamine and
triethylamine are useful in concentrations of about one-
half molar equivalent (3ml in the above table) to about
1 molar equivalent (6ml) with respect to the phosphate
ester. We may use the low molecular weight amines in
amounts from about one-fourth molar equivalent to about
1.5 molar equivalent or more.

In the following Table IV, ferric salts as shown were
used in combination with a standard 3 ml concentration of
phosphate ester solution, some with KOH and some without,
in 300 ml oil. The viscosity was measured with a #4
spindle at 10 rpm unless otherwise noted.

Table IV

Iron salt	ml Fe	Viscosity	Comment
Fe Citrate	3	6,800	
Fe Citrate	1	8,800	
Fe Citrate	3	16,700	
Fe Citrate	3	7,000+	
Fe Citrate	2	8,000	
Fe Citrate	2.5	3,300	#3 spndl; 10rpm
Fe Citrate	2.5	3,200	"
Fe Citrate	2.5	3,200	"
Fe Citrate	2.5	2,700	"
Fe Amm Sulf	1	13,000	
Fe Amm Sulf	1	3,500	(20 rpm)
Fe Amm Sulf	1.5	14,700	
Fe Amm Sulf	1.5	15,000	
Fe Chloride	3	6,200	
Fe Chloride	2	7,600	
Fe Sulfate	1	9,700	
Fe Sulfate	1.5	14,000	
Fe Sulfate	1	7,000	
Fe Amm Citrate	3	12,000	
Fe Gluconate	3	4,600	

Additional tests and demonstrations were made on

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combinations of ferric sulfate and low molecular weight amines. In the runs shown in Table V, Fann viscosity readings were taken on various gellant preparations including low molecular weight amines. For Table V, a solution (TC-23C) of 67% phosphate ester, 15% KOH and 18% solvent was prepared; this was mixed with a composition (TC-23E) comprising 54.4% ferric sulfate (40% solution) 15.9% triethanolamine, 18.7% ethylene glycol, 3% ammonium cumene sulfate, a surfacant (ACS) and 8% water. The shear rate in the Fann viscosimeter was maintained at 100± 0.1. The temperature was elevated as shown in the table. The gel achieved a remarkably stable viscosity after about 30 minutes of shear.

Table V

ELAPSED TIME Min.	SHEAR STRESS LB/100F^2	VISCOSITY (cP)	TEMP.°F
0	70.1	0	71
3	123.8	348	94
8	133.7	376	181
13	124.4	350	224
18	100.7	283	251
23	89.5	252	268
28	81.5	229	279
33	77.1	217	288
38	76.0	214	295
41	75.1	211	299
46	74.6	210	301
51	75.1	211	301
55	74.6	210	300
60	74.6	210	300
65	74.8	210	299
69	75.1	211	299
74	74.8	210	299
79	74.9	210	299
99	74.9	211	299

Table VI shows results using the same materials, in which the pressure was maintained at 240 psig (± 2) throughout. The shear rate was 100 ± 0.1 as in Table V.

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Table VI

	ELAPSED TIME Min.	SHEAR STRESS LB/100F^2	VISCOSITY (cP)	TEMP. °F
5	0	77.1	0	109
	4	120.6	339	144
	9	126.9	357	168
	14	138.1	388	185
10	19	150.9	424	196
	24	157.8	444	203
	29	157.2	442	210
	34	152.0	427	216
	39	145.4	409	222
15	44.5	139.4	392	227
	47.5	136.4	384	229
	52.5	133.9	377	230
	57.5	130.8	368	231
	61.5	111.6	314	231
20	66.5	86.8	244	230

A third series of results was obtained on the same preparation, as shown in Table VII:

Table VII

	ELAPSED TIME Min.	SHEAR STRESS LB/100F^2	VISCOSITY (cP)	TEMP. °F	PRESS (psig)
25					
	0	77.4	0	81	259
30	1	144.5	406	90	259
	11	174.5	491	136	261
	21	214.8	604	155	263
	31	213.6	601	168	264
	24	201.5	567	177	265
35	29	197.2	554	179	266
	58	196.7	553	180	266
	68	198.7	559	179	267
	86	200.5	563	179	268
	109	200.8	564	180	269
40					

These also were highly stable after a prolonged period.
In Table VIII, a gellant was prepared by mixing two
components - the first was 67% phosphate ester, 6% KOH,
and 27% solvent; the second was 54.4% ferric sulfate,
20.9% triethanolamine, 18.7% ethylene glycol, 3% ammonium
cumene sulfate (a surfactant) and 3% water. These two
components were mixed into Diesel oil at a concentration
of 2 components of 1%. The resulting gelled hydrocarbon
was tested in the Fann (model 50), viscometer in a manner

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similar to the above. For the series reported in Table VIII, the pressure increased gradually from 259 to 267 psig.

Table VIII

ELAPSED TIME Min.	SHEAR STRESS LB/100F^2	VISCOSITY (cP)	TEMP.°F
0	70.6	0	130
5	191.1	538	151
10	194.7	547	160
15	197.6	555	167
20	201.2	566	172
25	202.8	570	177
28	202.2	569	179
33	199.2	560	181
38	194.5	547	182
55	182.2	512	181
100	173.4	488	179

The same compositions used for Table VIII were run again for the results in Table IX. In this case, the pressure was maintained at 244-245 psig.

Table IX

ELAPSED TIME Min.	SHEAR STRESS LB/100F^2	VISCOSITY (cP)	TEMP.°F
0	74.2	0	105
1	172.0	484	129
5	159.8	449	183
9	124.9	351	218
16	92.6	260	255
24	78.2	220	277
32	74.8	210	290
38	73.9	208	298
46	73.9	208	300
52	73.9	208	300
56	73.9	208	300
82	73.8	208	299
112	73.8	208	299

The same compositions used for Tables VIII and IX were used for Table X. In Table X, the pressure dropped gradually from 240 psig to 237 psig. As in all Tables V - IX, the shear rate was maintained at 100 ± 0.1.

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Table X

ELAPSED TIME Min.	SHEAR STRESS LB/100F²	VISCOSITY (cP)	TEMP.°F
0	72.3	0	103
4	179.0	503	143
8	172.0	484	164
12	162.3	456	179
16	149.2	420	190
20	136.4	384	198
24	124.2	349	206
28	114.7	322	212
32	105.2	296	218
36	102.0	287	219
40	96.4	271	223
44	92.6	260	228
48	91.3	257	231
52	90.0	253	233
56	90.1	253	233
60	89.8	252	233
77	92.8	261	233
92	94.8	267	229
107	96.3	271	229
122	98.0	276	229

Excellent gels have also been made using the techniques recited below:

In this procedure, 55g ferric sulfate was blended with 11g monoisopropyl amine

$$H_2N-CH_3 \begin{array}{c} CH_3 \\ | \\ \\ | \\ CH_3 \end{array}$$
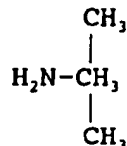
for a period of about an hour, then blended into Diesel oil containing a previously prepared mixture consisting of 67% phosphate ester, 15% KOH, and 18% solvent. The ferric sulfate - containing blend and the phosphate ester blend each comprised about 0.5 percent of the final fracturing fluid. The fracturing fluid was found to make a good gel overnight. A similar experiment substituting monobutyl amine provided an excellent gel overnight.

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Claims

1. Composition for fracturing formations comprising a hydrocarbon fracturing fluid and (a) about 0.3% to about 1.5% by weight of a phosphate ester of the formula HPO_4RR', where R is an alkyl, aryl, alkoxy, or alkaryl group having from 6 to about 18 carbon atoms and R' is hydrogen or an aryl, alkaryl, alkoxy, or alkyl group having from 1 to about 18 carbon atoms , (b) a ferric salt in an amount sufficient to form a gel with said hydrocarbon fluid and said phosphate ester, (c) a low molecular weight amine of the formula $H_{3-n}N(C_mH_{2m}R)_n$ where n is an integer from 1 to 3, each m is independently an integer from 2 - 6, and R is H or OH in an amount from about one-fourth molar equivalent to about one and one-half molar equivalent of the phosphate ester, and (d) up to about 10% surfactant.

2. Composition of claim 1 including a minor amount of KOH.

3. Composition of claim 1 wherein said low molecular weight amine has the formula $N(CH_2CH_2R)_3$ where R is H or OH.

4. Composition of claim 1 wherein said low molecular weight amine is present in an amount from one-half molar equivalent to one molar equivalent of the phosphate ester.

5. Composition of claim 1 wherein said low molecular weight amine is triethanolamine.

6. Method of claim 1 wherein said low molecular weight amine is triethylamine.

7. Composition of claim 1 wherein said ferric salt is present in an amount providing from 0.1 to 1.5 mole

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of ferric iron for each mole of phosphate ester.

8. Composition of claim 7 where in said ferric salt is present in an amount providing from about 0.8 to 1.2 mole of ferric iron for each mole of phosphate ester.

9. Composition of claim 1 wherein said ferric salt is ferric sulfate.

10. Composition of claim 1 wherein said surfactant is present in an amount from about 0.1% to about 10% of said composition.

11. Method of making a viscous hydrocarbon fracturing fluid comprising blending (a) a mixture of a phosphate ester, potassium hydroxide and a solvent with (b) a co-reacted mixture of an iron salt and a low molecular weight amine, in a hydrocarbon fracturing fluid.

12. Method of claim 11 wherein said phosphate ester is within the general formula HPO_4RR' where R is a straight or branched chain alkyl, aryl, alkoxy, or alkaryl group having about 6 to about 18 carbon atoms and R' is hydrogen or an aryl, alkaryl, alkoxy, or alkyl group having up to about 18 carbon atoms.

13. Method of claim 11 wherein said iron salt is ferric sulfate.

14. Method of claim 11 wherein said low molecular weight amine is triethanolamine.

15. Method of claim 11 wherein the molar ratio of iron to phosphate is 0.25:1 to 1.5:1.

16. Method of claim 11 wherein the molar ratio of ferric salt to amine is 0.1:1 to 1.5:1.

INTERNATIONAL SEARCH REPORT

A. CLASSIFICATION OF SUBJECT MATTER
IPC(6) :C09K 7/06
US CL :106/285, 287.18; 507/128, 922
According to International Patent Classification (IPC) or to both national classification and IPC

B.   FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. :   106/285, 287.18; 507/128, 922

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

  NONE

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

  NONE

C.   DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 5,271,464 A [MCCABE] 21 DECEMBER 1993, see entire document	1-16
A	US 3,575,859 A [MONROE] 20 APRIL 1971, see entire document	1-16
A	US 3,338,935 A [KERSCHNER ET AL] 29 AUGUST 1967, see entire document	1-16

☐ Further documents are listed in the continuation of Box C.   ☐ See patent family annex.

* Special categories of cited documents:	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"A" document defining the general state of the art which is not considered to be of particular relevance	
"E" earlier document published on or after the international filing date	"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"O" document referring to an oral disclosure, use, exhibition or other means	
"P" document published prior to the international filing date but later than the priority date claimed	"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
14 MARCH 1997	**0 8 MAY 1997**

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